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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Studless Pneumatic Tire

average length = 100-5000μ

average diameter ≥ 1μm

aspect ratio = 10-1000

(length/diameter)

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ABSTRACT OF THE DISCLOSURE

A studless pneumatic tire is disclosed which comprises a tread compound formed from a cellular rubber and short fibers of a specified average length and a specified average diameter distributed and specifically oriented within the cellular rubber which has a selected set of physical properties. The tire exhibits enhanced all-weather driving performance.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to pneumatic tires suitable for use in automotive vehicles and more particularly to such a tire capable of enhanced driving performan :e under all-weather conditions.

Description of the Prior Art

In snowy and icy season, automobile cars have been assembled usually with a spiked tire or a tire chain. Such antiskid devices, when brought into severe abrasive contact with a paved normally dry or wet road surface, would tend to damage the road, kicking up dusts or surface debris which eventually poses an environmental pollution problem.

Studless tires have of late become prominently popular for their improved braking and ride qualities and are beginning to take the place of conventional spiked or chained tires.

There have already been introduced a number of studless tires as disclosed for example in Japanese Patent Laid-Open Publication Nos. 62-283001 and 63-90402, which studless tires feature the use of cellular rubber of a closed-cell structure for the tread of the tire. Such prior studless tires are satisfactory in terms of frictional force directed onto icy or snowy roadway, but not quite satisfactory in edging and draining effects so that their wear-resistant property and driving performance on normally dry or wet roadway tend to decline.

There are known two forms of frictional forces exerted on the tire during its rolling along an icy or snowy road; one is called a plowing frictional force and the other an adhesive frictional force. Rubber blends therefore hold an important role in obtaining a maximum effect of these frictional forces. A relatively high rigidity of tread rubber block in the circumferential direction of the tire is required to provide increased edging effect. On the other hand, a rigidity radial of the tread block facing at right angles to an icy road surface is required to be rather low so as to obtain sufficient adhesive frictional force. Attempts have been made to cope with this problem by incorporating short fibers in cellular rubber for the tread to increase its hardness as disclosed for example in Japanese Patent Laid-Open Publication No. 63-89547. However, due to short fibers being randomly distributed in the rubber, the rigidity of the tread block tends to increase uniformly throughout the tread and does not increase more circumferentially than radially of the tire. Therefore, no appreciable adhesive effect or on-ice frictional force of the tire can be expected.

Generally, poor driving performance of studless tires under normal road surface conditions (dry or wet) is chiefly attributed to the glass transition temperature Tg of certain polymers used as the tire tread compound. Such polymers are required to have a relatively low Tg with a view to retaining adequate elasticity at low ambient temperature.

For this reason, wide use has thus far been made of typically natural rubber (NR), polybutadiene rubber (BR) and low styrene content styrene-butadiene rubber (SBR) for studless tires. Since the frictional force of rubber exerted on a dry or wet roadway is largely dependent upon the loss tangent of rubber at about 0°C, it is desirable to use such a polymer which has a viscoelastic transition in the neighborhood of 0°C; i.e. polymers having a relatively high glass transition temperature Tg. Tires with the particular emphasis on gripping force are therefore fabricated in most cases from SBR having increased styrene contents and higher Tg. Since thus there are different parameters related to the glass transition temperature Tg of polymers, it has been difficult to find a tire tread compound which ensures sufficient gripping force on both icy-snowy and dry or wet road surfaces as well as freedom of wear on contact with dry or wet roadway.

SUMMARY OF THE INVENTION

It is therefore a primary object of the present invention to provide a studless pneumatic tire which has improved all-weather driving performance and braking capabilities under icy and snowy road conditions.

This object is achieved according to the invention by the provision of a studless pneumatic tire having a tread which is formed from a cellular rubber and short fibers distributed therein, characterized in that the cellular rubber contains a polymer having a glass transition

temperature in the range of from -60°C to -20°C and a urea-based additive blended in less than an equivalent ratio with a blowing agent; the cellular rubber has an average cellular area $\overline{X}$ over a sectional surface of the tread in the range of 100 - 5,000 μm2; the cellular rubber has a variation coefficient K of its cellular area in the range of 0.5 - 0.8; the cellular rubber has a cellular occupancy rate in the tread in the range of 10 - 40; and a majority of the short fibers are oriented to extend circumferentially internally of the tire tread along the ground contacting surface and side walls of each tread block.

With cellular rubber having a uniform rigidity distribution it is difficult to provide an improvement in both edging effect and adhesive frictional force of the tread relative to the ground. It is known that the elastic modulus of rubber increases in a direction parallel to the orientation of short fibers unidiretionally laid in the rubber but does not appreciably change in a direction at right angles to the fiber orientation. This anisotropy of fiber reinforced rubber can be thus utilized in controlling the orientation of short fibers to be directed in a direction parallel to the surface of the tread block so that its rigidity will decrease in a direction at right angles to the block surface and conversely increase in a direction parallel to the block surface, thereby achieving a maximum effect of edging and adhesive frictional force both at the same time.

Typical examples of polymeric compound for the tread of a studless tire include NR having a low glass transition temperature Tg of less than -60°C, SR having low styrene contents. Polymers with Tg of less than -60°C according to Laid-Open Disclosures 62-283001 and 63-90402 are recommendable as they can retain sufficient elasticity at temperatures at which the studless tire is used. Considering tire performance on dry or wet road, however, polymers with too low Tg are not desirable.

It is considered essential to increase the loss of hysteresis tan δ of the tread compound so as to improve on-road tire performance. Since the tread rubber during running of the tire at normal driving speed on a dry or wet road undergoes vibration of the order of several thousands hertzs (Hz), it is a common practice to measure the tan δ of a given tread compound at 0°C in the region of transition from a glass-like state to a rubbery state. This transition region has a temperature band of about 30°C from the glass transition temperature to the highest point. It follows that the peak of tan δ of the polymer appears at 0°C within that transition temperature band. In other words, it is preferred to use a class of polymers for the tire tread which have a relatively high glass transition temperature Tg for enhanced tire performance on dry and/or wet road, but conversely the tire would be liable to grow stiff on contact with icy and/or snowy road and therefore decline in braking effect.

It has been found that the use of cellular rubber even in small amounts in the fabrication of studless tires is highly conducive to preventing high Tg polymers from becoming unduly hard at low temperature. The features of such cellular rubber are well disclosed in Japanese Laid-Open Disclosure No. 1-103501. Cellular rubber alone however cannot maintain the requisite block rigidity of the tire tread at increased temperature, but the use of cellular rubber coupled with specifically oriented short fibers can control the anisotropy of the rigidity of the tread block to permit the use of relatively low modulus compounds.

The above and other advantages and features of the invention will appear apparent from the following detailed description taken in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view taken in half along the meridian line of a tire constructed in accordance with the invention;

FIG. 2 is a diagrammatic plan view of a tread portion of the tire; and

FIG. 3 is a cross-sectional view taken on the line III - III of FIG. 2.

DETAILED DESCRIPTION OF THE INVENTION

Referring to the drawings and FIG. 1 in particular, there is shown a studless pneumatic tire 100 embodying the invention, the tire 100 comprising a pair of spaced beads

101, 101, a pair of side walls 102, 102 extending radially inward to join the respective beads 101, 101, a tread 103 interposed between the side walls 102, 102, a carcass 104 extending between the beads 101, 101 and a belt structure 105 surrounding the inner peripheral wall of the tread 103. Designated at 106 is the outer surface of the tread 103.

The present invention relies on the following combination features which constitute the essential requirements of the inventive studless tire for achieving the aforesaid object.

(1) The tread 103 is formed from a cellular rubber and short fibers, the rubber containing a polymer having a Tg of from -60°C to -20°C and having a urea-based additive blended in less than an equivalent ratio with a blowing agent.

Polymers should have a glass transition temperature Tg of higher than -60°C to ensure sufficient gripping power of the tire tread on dry or wet roadway. With Tg above -20°C, the tire is liable to become objectionably hard even at room temperature and decline in its gripper power. Examples of the polymer eligible for the purpose of the invention include SBR having increased styrene content or increased vinyl component in the butadiene, BR and butyl rubber having increased vinyl component. These polymers are blended in an amount of 30 - 70 parts by weight per 100 parts by weight of total rubber. Less than 30 weight parts polymer would degrade the tire performance on dry or wet road, whilst more

than 70 weight parts would lead to objectional hardening or stiffening of the tire at low temperature and hence to insufficient gripping power of the tire on icy or snowy road. The remainder of 70 - 30 weight parts may be diene-based rubber of Tg below -60°C such as NR, cis component-rich BR and low styrene content SBR.

It has been found that a closed-cell structure in cellular rubber greatly contributes to enhanced edging and draining effects of the tire particularly on the ice which assumes a pseudoliquid phase at about 0°C. It has now been further found that these effects are pronounced with use of a relatively high hardness cellular rubber for the tread, contrary to the conventional notion that on-ice or on-snow frictional force of the tread can be improved by the use of rubber of lower hardness at lower temperature. Cellular rubber is known to decline considerably in hardness compared to non-cellular rubber. Therefore, matrix rubber must be chosen with higher hardness typically for example by using increased amounts of carbonblack and other reinforcing materials or reduced amounts of oil and other softening agents. This will however invite rubber processing difficulty and aggrevated heat generation. Noting that urea-based additives have a contributory effect upon the increase in the crosslinking density of a starting rubber, extensive investigation has been made to indicate that such contributory effect can be much more enhanced by using a urea-based additive in combination with a blowing agent than

introducing urea alone into the rubber composition. It has now been found that urea-based additives when added in specified blend ratios with blowing agents to prepare a cellular rubber compound will suppress a decline in the hardness of the rubber due to blowing and ensure a hardness comparable to non-cellular rubber without adverse effect upon rubber processing or heat generation. The use of a urea-based additive is also effective in that it serves as an acceptor for malodorous formaldehyde which is formed during decomposition of a blowing agent such as nitroso compounds.

As already mentioned hereinabove, with cellular rubber having a uniform rigidity distribution it is difficult to provide an improvement in both edging effect and adhesive frictional force of the tread relative to the ground. It is known that the elastic modulus of rubber increases in a direction parallel to the orientation of short fibers unidirectionally laid in the rubber but does not appreciably change in a direction at right angles to the fiber orientation. This anisotropy of fiber reinforced rubber can be thus utilized in controlling the orientation of short fibers to be directed in a direction parallel to the surface of the rubber block so that rigidity will decrease in a direction at right angles to the block surface and conversely increase in a direction parallel to the block surface, thereby achieving a maximum effect of edging and adhesive frictional force both at the same time.

The urea-based additive according to the invention is used preferably in an amount of 30 - 90 weight percent based on the blowing agent. Amounts of the urea-based additive greater than those of the blowing agent lead to saturation of the desired effect, hence would be only economically infeasible and would furthermore invite undue reduction of the decomposition temperature depending upon the type of blowing agents used, most likely resulting in unvulcanized rubber being blown in the mixing and extruding operation.

(2) <u>An average cellular area $\bar{X}$ over a sectional surface of the tread is in the range of 100 - 5,000 μm^2.</u>

The cellular rubber to be used according to the invention is of a closed-cell structure having an average cellular area of 100 - 5,000 μm^2, preferably 500 - 3,000 μm^2. Cellular areas less than 100 μm^2 provide insufficient improvement in on-ice or on-snow tire performance, whereas more than 5,000 μm^2 give rise to wear resistance and poor driving performance of the tire.

(3) <u>A variation coefficient K of the cellullar area $\bar{X}$ in the tread is in the range of 0.5 - 0.8.</u>

It has now been found that a relatively narrow distribution width of the cellular structure, a cellular shape and an optimized cellular occupancy rate have an important bearing upon all-weather tire performance.

The term variation coefficient K as used herein is derived from the formula

$$K = S/\bar{X}$$

where $\bar{X}$ is an average cellular area (μm^2) and S is a standard deviation of $\bar{X}$.

The variation coefficient K should be in the range of 0.5 - 0.8. Smaller values than 0.5 would result in reduced edging effect of the tire, while larger than 0.8 would lead to reduced draining effect.

(4) <u>A cellular occupancy rate in the tread is in the range of 10 - 40%.</u>

The term cellular occupancy rate is used to designate a rate of cellular area per unit area of the rubber.

Cellular occupancy rates are higher the better for on-snow or on-ice tire performance and would be about 10% - 20% in consideration of the use of cellular rubber for studless tires. However, such a tire is highly susceptible to wear on contact with a dry, particularly hot road surface during summer season and therefore can be used only on icy and/or snowy road during winter season. No appreciable improvement can be expected from varying the rate of carbonblack. The reason that a tire tread formed from cellular rubber having a higher cellular occupancy rate exhibits enhanced gripping power relative to snowy or icy roadway is attributed to the fact that the cells in the inner layer of the tire show themselves up on the tread surfaces as the tread progressively wears and provide increased coarse surface area or true contact surface area to remove water film on the road.

Surprisingly, cellular rubber with as small a cellular

occupancy rate as it can be effectively used according to the invention which is intended to provide a tire made from cellular rubber containing a highly [illegible] and yet capable of retaining adequate elasticity. Greater than 40% cellular occupancy rates would lead to faster wear of the tire on dry road.

(5) A majority of short fibers are oriented to extend along the ground contacting surface and side wall surfaces of a tread block 107.

Reference to FIGS. 2 and 3 shows the distribution of short fibers 108 in a celluar rubber 109 in which the fibers 108 are oriented circumferentially in the direction of E - E along the ground contacting surface 107a and the side wall surfaces 107b of the tread block 107. This fiber orientation ensures retention of greater rigidity of the tread blocks circumferentially than radially of the tire thereby providing increased adhesive and frictional effect relative to an icy road surface. The depicted orientation of the fibers 108 can be obtained during vulcanization of the tire in the mold due to the inherent tendency of the fibers 108 to follow the flow of rubber. However, care must be taken to choose a proper fiber length as too short fibers tend to move objectionably randomly. Therefore, the short fibers 108 to be used in the invention are preferably greater than 100 μm in average length, preferably in the average length range of 100 - 5,000 μm, more preferably 1,000 - 3,000 μm. The average diameter of the short fibers

108 is preferably greater than 1 μm. In the case of cross-sectionally non-circular short fibers, the average diameter is a mean value of the maximum and the minimum diameter. The length/diameter ratio of the fibers is preferably from 10 to 1000. The short fibers 108 may be those of cotton, silk and other natural fibers, or cellulose, polyamide, polyester, polyvinyl alcohol and other chemical synthetic fibers and carbon.

The invention will be further described by way of the following examples.

Inventive Examples 1 - 4, Comparative Examples 1 - 6 and Reference Examples 1 and 2

Various sample tires of 185/70 R13 85Q having the constituent compositions shown in Table 1 were subjected to the following tests conducted on 1600 cc FF car.

Average cellular area X, variation coefficient K and cellular occupancy rate

A test piece was cut out from each sample tire tread and projected to an image magnified 165 times by NEXUS6400 of Kashiwagi Research Institute. Test results were averaged out of ten (10) such test pieces.

On-ice braking performance

A braking distance was measured upon braking after the car was started at 30 km/hr. on ice board. A reference value of 100 for conventional tire (control) was taken as an index. Braking effect is better the larger the index value.

On-snow driving performance

Snow on paved road was compressed and made slippery by applying a brake repeatedly on the car. Climbing test was conducted on such slippery road at 5% (2.9°) slope and acceleration time was measured from zero start over a travel distance of 30 meters. Control tire was taken as a reference for index display of the test results on each sample tire. Driving performacne is better the larger the index value.

On-wet road braking performance

A braking distance was measured after the car was started at 40 km/hr on watered asphalted road. A reference value of 100 for conventional tire (control) was taken as an index. Braking effect is better the larger the index value.

Wear resistance (on dry road)

After a travel of the test car for 20,000 killometers under JATMA standard load and air pressure conditions, the sample tires were checked for wear. The amount of wear for each sample tire was indexed against control tire. Wear resistance is better the larger the index value.

Dynamic Young's modulus MPa

Test piece was cut out from both the outer surface and interior of each sample tread block circumferentially of the tire. The test piece measuring 5 mm wide, 2 mm thick and 20 mm in interchuck length was tested under conditions of 20 Hz frequency, 10% initial strain, ± 2% dynamic strain

and 0°C temperature. Rigidity of the tread is higher the greater the measured value.

In Table 1, the control tire is a conventional studless tire without cellular rubber and short fibers. Inventive Examples 1 - 4 respectively represent the tires of the invention which incorporate the specified combination cellular rubber/short fiber tread structure having satisfactory all-weather tire performance. The tire of Comparative Example 1 incorporating cellular rubber containing low Tg polymer is satisfactory for on-ice and on-snow performance but not for normally dry and wet road performance. The tires of Comparative Examples 2 and 3 contain polymer of Tg and fiber orientation both conforming to the inventive range but have a tread compound of greater cellular rate or porosity. They are satisfactory in terms of on-ice and on-snow driving and braking on wet road, but are highly susceptible to wear.

The tire of Comparative Example 4 comprising a cellular rubber/short fiber combination contains fibers of too small length which are randomly oriented with resultant elastic modulus being substantially uniform through the center and outer layers of the tread block, leading to poor on-snow/or ice tire performance. Reference Example 1 is provided to demonstrate unsatisfactory on-snow/ice tire performance with too short average length fibers (10 μm) and Reference Example 2 to demonstrate tire performance only comparable to conventional tires if the fibers are too long (8,000 μm).

Table 1

	control	Comparative Example 1	Inventive Examples 1	Inventive Examples 2	Comparative Examples 2	Comparative Examples 3	Comparative Examples 4
polymer NR	60	60	60	60	60	60	60
polymer SBR1 *1	-	-	40	-	40	40	40
polymer SBR2 *2	-	-	-	40	-	-	-
polymer BR *3	40	40	-	-	-	-	-
carbonblack	75	75	75	75	75	75	75
oil	18	18	18	18	18	18	18
stearic acid	3	3	3	3	3	3	3
ageing inhibitor	2	2	2	2	2	2	2
zinc white	3	3	3	3	3	3	3
wax	1	1	1	1	1	1	1
sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
vulcanization accelerator	1	1	1	1	1	1	1
short fiber A *4	-	5	5	5	5	5	-
short fiber B *5	-	-	-	-	-	-	5
short fiber C *6	-	-	-	-	-	-	-
short fiber D *7	-	-	-	-	-	-	-
short fiber E *8	-	-	-	-	-	-	-
adhesive-additive *9	-	1	1	1	1	1	-
blowing agent *10	-	2	2	2	3	3.5	2
urea-based additive *11	-	1	1	1	2	3	1
average cellular area [µm²]	-	1000	900	900	1500	3000	1200
cell variation coefficient	-	0.55	0.50	0.50	0.55	0.60	0.40
cellular occupancy [%]	-	3	4	3	7	12	3
dynamic Young's modulus							
(center) [MPa]	6.3	5.9	6.8	7.0	6.8	6.5	7.0
(surface) [MPa]	6.3	6.6	7.5	7.5	7.3	7.2	7.0
braking (on ice)	100	105	103	101	105	110	100
driving (on snow)	100	105	108	110	115	115	105
braking (wet road)	100	98	110	115	115	120	95
wear resistance	100	95	105	103	95	80	95

Table 1 (cont'd)

	Reference Example 1	Inventive Example 3	Reference Example 2	Inventive Example 4
polymer NR	60	60	60	60
polymer SBR1 *1	40	40	40	40
polymer SBR2 *2	-	-	-	-
polymer BR *3	-	-	-	-
carbonblack	75	75	75	75
oil	18	18	18	18
stearic acid	3	3	3	3
ageing inhibitor	2	2	2	2
zinc white	3	3	3	3
wax	1	1	1	1
sulfur	1.5	1.5	1.5	1.5
vulcanization accelerator	1	1	1	1
short fiber A *4	-	-	-	-
short fiber B *5	-	-	-	-
short fiber C *6	5	-	-	-
short fiber D *7	-	5	-	20
short fiber E *8	-	-	5	-
adhesive-additive *9	-	-	-	-
blowing agent *10	2	2	2	2
urea-based additive *11	1	1	1	1
average cellular area [μm²]	900	900	900	800
cell variation coefficient	0.52	0.50	0.49	0.51
cellular occupancy [%]	4	4	4	3
dynamic Young's modulus				
(center) [MPa]	7.2	6.8	7.2	7.7
(surface) [MPa]	7.5	7.5	7.5	15.8
braking (on ice)	98	105	99	103
driving (on snow)	100	110	100	115
braking (wet road)	102	108	100	110
wear resistance	100	105	98	101

Note: *1 ... styrene contents 14.1 wt%, vinyl component in butadiene 30 wt% and Tg -56°C

*2 ... styrene contents 23.5 wt%, vinyl component in butadiene 18 wt% and Tg -53°C

*3 ... cis component 98 wt% and Tg -53°C

*4 ... cellulose short fibers (Santoweb D by Nihon Monsant)
1500 μm in average length, 12 μm in average diameter (longest 16 μm and shortest 8 μm)

*5 ... carbon short fibers, 5 μm in average length, 1 μm in average diameter

*6 ... nylon short fibers, 50 μm in average length, 10 μm in average diameter

*7 ... nylon short fibers, 1500 μm in average length, 10 μm in average diameter

*8 ... carbon short fibers, 8000 μm in average length, 10 μm in average diameter

*9 ... hexa-methoxy-methyl melamine (Regimen 3520 by Nihon Monsant)

*10 ... dinitroso-pentamethylene tetramine (Cellular D by Eiwa Chemical)

*11 ... urea compound (Cellpaste K5 by Eiwa Chemical)

WHAT IS CLAIMED IS:

1. A studless pneumatic tire comprising a tread having a plurality of blocks formed from a cellular rubber and short fibers distributed therein, said cellular rubber containing a polymer having a glass transition temperature in the range of from -60°C to -20°C and a urea-based additive blended in less than an equivalent ratio with a blowing agent; said cellular rubber having an average cellular area $\overline{X}$ over a sectional surface of the tread in the range of 100 - 5,000 μm2; said cellular rubber having a variation coefficient K of its cellular area in the range of 0.5 - 0.8; said cellular rubber having a cellular occupancy rate in the tread in the range of 13 - 48; and a majority of said short fibers being oriented to extend circumferentially internally of the tread along the ground contacting surface and side walls of each tread block.

2. A studless pneumatic tire as defined in claim 1 wherein said short fibers have an average diameter of greater than 1 μm and an average length in the range of 100 - 5,000 μm.

3. A studless pneumatic tire as defined in claim 1 wherein said polymer is selected from the group consisting of styrene-rich SBR, vinyl-rich in butadiene SBR, vinyl-rich BR and butyl rubber.

4. A studless pneumatic tire as defined in claim 1 wherein said polymer is added in an amount of 30 - 70 parts by weight per 100 parts by weight of total rubber.

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FIG. 1

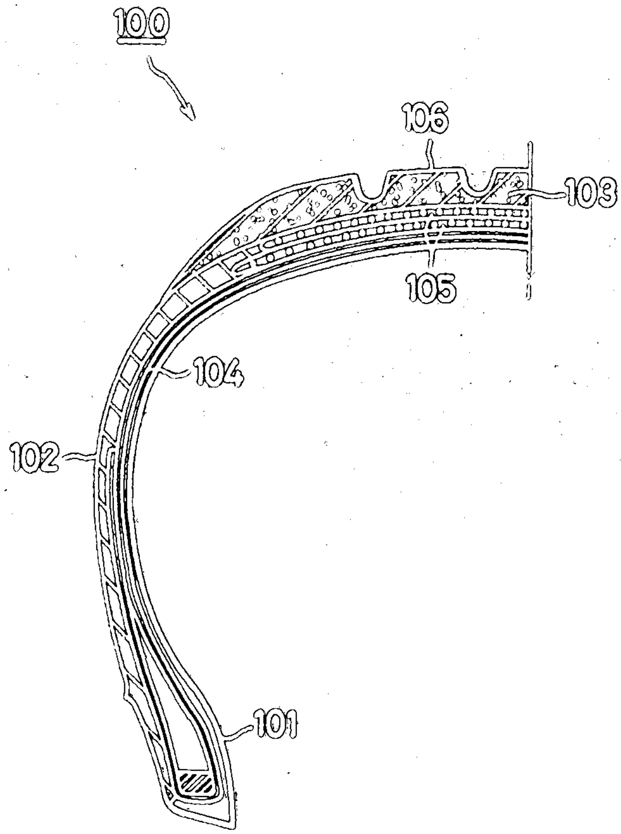

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FIG. 2

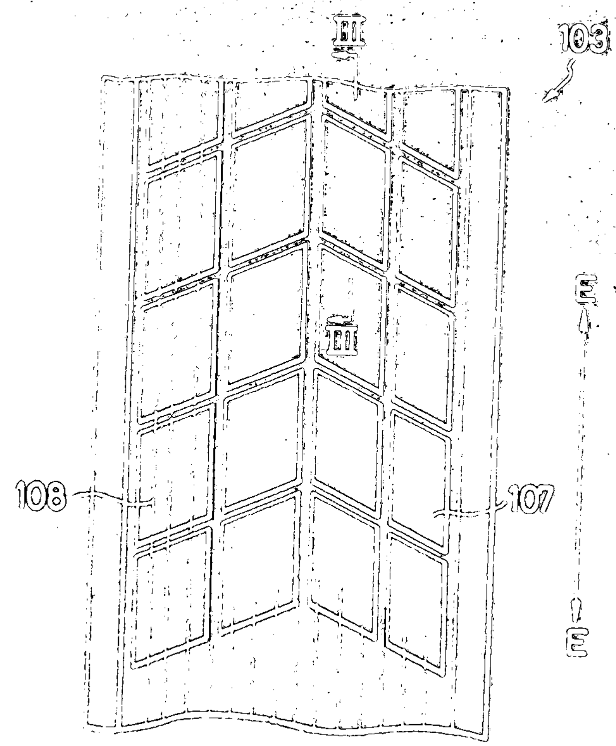

FIG. 3